

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Application of:

Shelby et al.

Serial No.: 10/743,488

Group Art Unit: 1713

Filed: December 19, 2003

Examiner: S. Sastri

For: BLENDS OF ALIPHATIC-AROMATIC COPOLYESTERS WITH
ETHYLENE-VINYL ACETATE COPOLYMERSCommissioner for Patents
P. O. Box 1450
Alexandria, VA 22313-1450**DECLARATION OF MARCUS DAVID SHELBY**

I, Marcus David Shelby, hereby declare as follows:

1. I am a named inventor on the above-identified application.
2. I have a Ph.D. degree in Chemical Engineering from Virginia Tech.
3. I am a Registered Professional Engineer (PE License 24108-E).
4. I have worked for Eastman Chemical Company in Kingsport, Tennessee from 1989 to the present, excluding the years 1992 to 1996 when I was on educational leave at Virginia Tech.
5. I have reviewed an English translation of JP 56-38367 A to Masuda et al. ("Masuda"). The aliphatic aromatic polyesters (AAPE) described in the current claims of the subject application are outside of the melt index range described in Masuda. In Masuda, the AAPE is defined as having a melt index (MI) in the 50 to 400 g/10min range, as measured at 140°C. In our current claims, we specify that the AAPE should have an inherent viscosity from about 0.8 to 1.6 dl/g. While these are two different methods for measuring "viscosity," the following analysis will show that the viscosity range for these two definitions do not overlap.

Definitions

6. Because there are various forms of viscosity, a few definitions are provided for clarification.

7. "Melt" Viscosity (also referred to as simply "viscosity"). This is defined as the shear stress exhibited by a molten polymer divided by the shear rate for the particular flow. Melt viscosity is a function of temperature, and is the most accurate measurement of the flow behavior of a polymer. It is typically measured using, for example, a parallel plate rheometer which gives viscosity data at different temperatures and for different shear rates. Although it is a more precise value, the equipment required is more expensive and time-consuming to use; therefore, it is rarely discussed in typical polymer datasheets. Units for melt viscosity are typically "poise" or "Pascal-s".

8. Melt Index (MI) (also referred to as "melt flow rate" or MFR). MI is a very simple test that is common with polyolefin manufacturers (e.g., ethylene vinyl acetate producers) and is depicted in Figure 1. It involves measuring the amount of polymer that is forced through a specified capillary tube at a given temperature, over a time period of 10 minutes. To perform the test, the capillary cell is charged with polymer and then allowed to heat up to the appropriate temperature. Once heated, a plunger assembly of a given weight is inserted which then forces the polymer through the capillary. The amount of material that is then extruded in 10 minutes is weighed and this value denoted as the "melt index." Melt index testing is standardized to various temperatures, capillary geometries, and applied weights, with 190°C and 2.16kg being the most common (the latter being described under ASTM D6340-98). Nevertheless,

there are some polymers where 190°C will not work well. For example, in Masuda, their olefin MI is measured at the standard 190°C, but their polyester MI is measured at 140°C. This is done because the polyester is an adhesive formulation and its viscosity is too low to be tested accurately at 190°C. In contrast, the polyesters of our invention are of higher viscosity and have been measured at 190°C. ***This difference in MI test temperature is the first indication that the polyesters of Masuda and our invention are significantly different with regards to viscosity.***

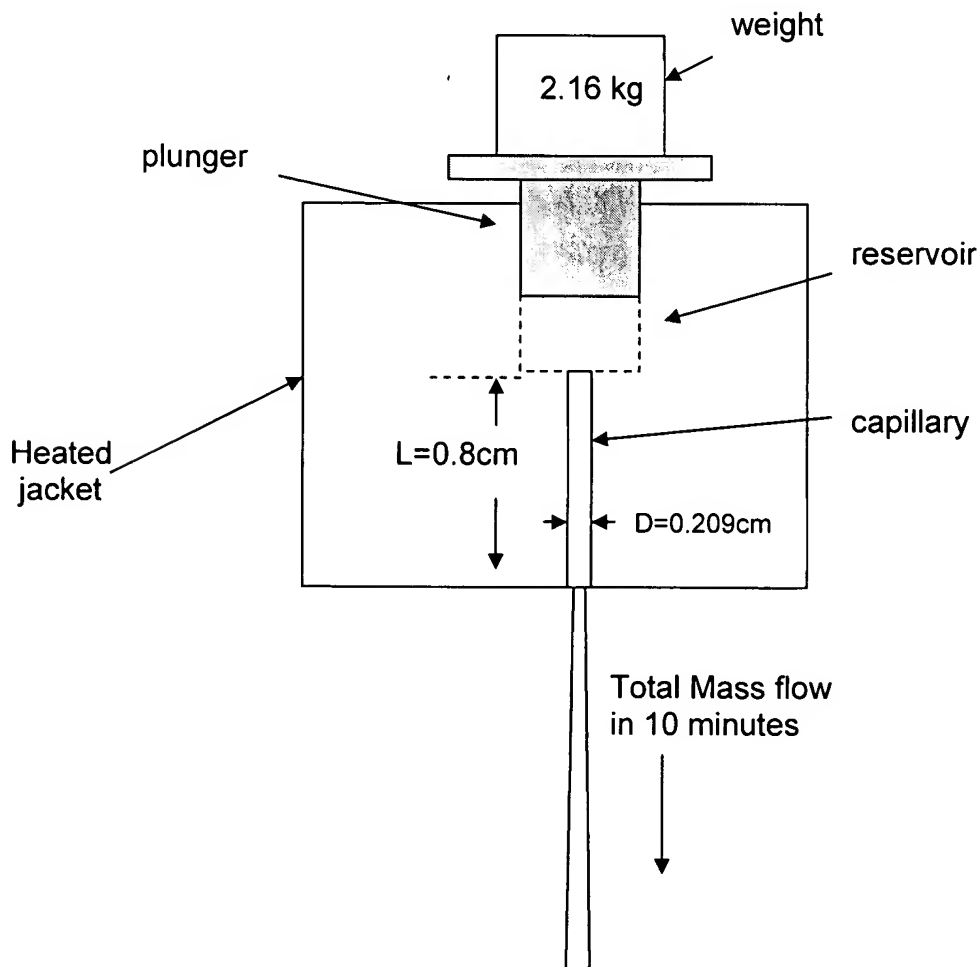


Figure 1. Schematic of a typical Melt Index test

9. It is also important to note that MI is *inversely proportional* to melt viscosity at the temperature being used. In other words, if one doubles the melt viscosity of the polymer, then the melt index will be cut in half because less material will flow out of the capillary. This will be made more clear in the derivation below. Units for MI are listed as "g/10 min."

10. Inherent or Intrinsic Viscosity (IV) – This test is very common with polyesters, but not polyolefins. It is important to note that it is NOT the same as melt viscosity or melt index. IV involves dissolving a very small amount of polymer in a good solvent (typically 0.5 wt% of polymer) and measuring the viscosity of the solution. These solution-type viscosity numbers provide a good indicator of the molecular weight of the polymer, assuming the polymer is adequately dissolved and swelled by the solvent. IV is very much dependent, however, on the polymer and solvent system used (the fact that most polyolefins are not easily dissolved in common solvents explains why IV is not commonly used). Typically, an increase in IV corresponds with an increase in melt viscosity, but the relationship is not linear. Instead, for most polyesters, we find that viscosity theoretically should vary in proportion to $IV^{5.1}$ (i.e., IV raised to the 5.1 power) and this trend is found to agree well with experimental data. Similarly, MI should therefore vary approximately in proportion to $IV^{-5.1}$ given the inverse relation with viscosity. Units for IV are typically "dl/g."

Conversion of AAPE IV Data to Melt Index

11. As stated previously, polyester manufacturers typically "describe" their materials in terms of IV, not melt index, so the appropriate conversions need to be

made for comparison. Figure 2 shows experimentally measured melt index data for a series of AAPE of different IVs. Note that the melt index data is at the more standard 190°C test temperature, not 140°C. At the time these measurements were originally made, there was no need to use the less common 140°C test condition as it was considered less accurate and inappropriate given the high viscosity of the resins tested. While the preferred approach for this document would be to go back and remeasure the previous samples at 140°C, these samples were unfortunately no longer available. At the time of this writing, only one IV sample was still available to measure at both 140°C and 190°C so we have to rely on the theoretical basis described below to convert the other IV data to 140°C melt index.

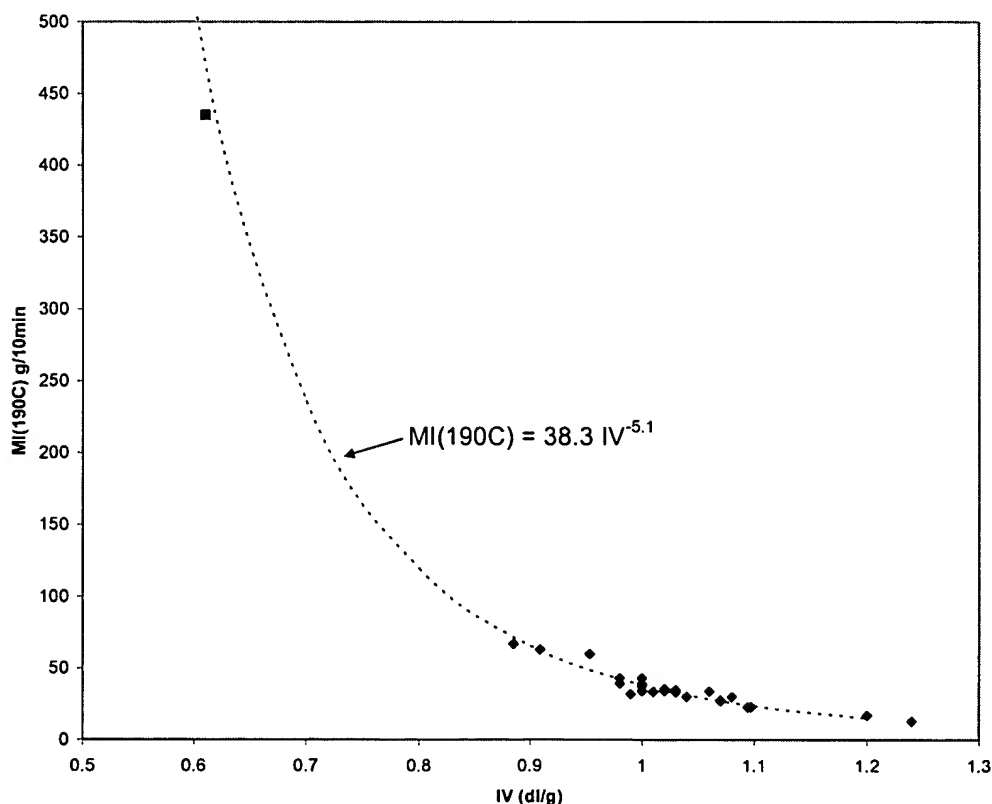


Figure 2. Melt Index at 190°C as a Function of IV

12. Inspection of the data in Figure 2 shows that the MI data is found to follow a power law trend with IV, and curve fitting of the data yields the following equation:

$$MI (@190^{\circ}\text{C}) = 38.3 IV^{-5.1} \quad (1)$$

where IV is the inherent viscosity and MI (@190°C) is the melt index measured at 190°C.

13. At this point, we have converted the IV data to melt index at 190°C, but we still need melt index at 140°C to compare with Masuda. To convert from MI at 190°C to MI at 140°C, we must look deeper at the flow behavior of the polymer in a tube. Assuming the melt viscosity is known, the melt index as a function of viscosity can be approximated from Poissuille's Law for flow in a tube as

$$MI(T) = \frac{1.8375 \times 10^7 \rho D^2}{\eta(T, \gamma, IV)} \left(\frac{W}{L} \right) \quad (2)$$

where (see also Figure 1 for definitions):

MI(T) = the melt index, or "mass flowrate per 10 minutes" at a test temperature T;

ρ = melt density in g/cm³ (ρ is approximately 1 g/cc for AAPE);

W = weight of test (2.16 kg);

L = length of capillary tube (L=0.8 cm);

D = diameter of capillary tube (D=0.209 cm); and

$\eta(T, \gamma, IV)$ = melt viscosity of polymer at temperature T and effective capillary shear rate γ .

Note that the above equation has been modified from the standard Poisseulle's law to reflect the 10 minute flow time, and to scale for the unit systems of the variables above (see "Polymer Viscoelasticity" by E. Riande et al., Marcel Dekker, NY, 2000, pg 521-523

for a summary of the general Poissuille's law for flow in a capillary). The above equation does not take into account the entrance and exit pressure drops in the capillary, but the error from neglecting these is small.

14. While we could use the above equations directly, it is easier if we can take advantage of the fact that all of the test variables including W, L, ρ , and D will be constant for both the 140°C and 190°C test. The ONLY variable that changes significantly is $\eta(T, \gamma, IV)$. So for 190°C, we have

$$MI(190^\circ C) = \frac{1.8375 \times 10^7 \rho D^2}{\eta(190^\circ C, \gamma, IV)} \left(\frac{W}{L} \right) \quad (3)$$

and for 140°C we have

$$MI(140^\circ C) = \frac{1.8375 \times 10^7 \rho D^2}{\eta(140^\circ C, \gamma, IV)} \left(\frac{W}{L} \right) \quad (4)$$

If we divide Equation (4) by Equation (3) and simplify, we get

$$\frac{MI(140^\circ C)}{MI(190^\circ C)} = \frac{\eta(190^\circ C, \gamma, IV)}{\eta(140^\circ C, \gamma, IV)} \quad (5)$$

since all of the other terms (e.g., W, D, L, and ρ) cancel out. Thus, Equation (5) gives us a way to calculate the melt index at 140°C from the MI at 190°C if the viscosity ratio between the two temperatures (i.e., 190°C and 140°C) is known.

15. While the viscosity $\eta(T, \gamma, IV)$ is a strong function of the temperature and IV and, to a lesser degree, the shear rate in the capillary, the viscosity ratio in Equation (5) is approximately constant, and independent of IV and shear rate. This is because the IV and shear rate components apply almost equally to both the numerator and denominator of (5) and effectively cancel out. For example, polymers in general are

known to follow a viscosity-temperature behavior defined by the Arrhenius type equation:

$$\eta(T, IV) = A \exp\left(\frac{E_a}{RT}\right) \quad (6)$$

where A is the “front factor,” E_a is the activation energy, R is the universal gas constant, and T is the temperature (in Kelvin). The activation energy E_a (or E_a/R) is not a function of IV or molecular weight, but is a constant depending on the chemical nature of the polymer. Only the front factor A varies as the IV changes. However, if we take the viscosity ratio between two temperatures as in Equation (5), we can eliminate this IV dependence. For example, at different temperatures T_1 and T_2 :

$$\eta(T_1, IV) = A \exp\left(\frac{E_a}{RT_1}\right) \quad (7)$$

$$\eta(T_2, IV) = A \exp\left(\frac{E_a}{RT_2}\right) \quad (8)$$

Dividing Equation (7) by Equation (8) yields the viscosity ratio:

$$\frac{\eta(T_1, IV)}{\eta(T_2, IV)} = \exp\left(\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right) \quad (9)$$

Note that the front factor A cancels out in Equation (9), so the viscosity ratio, and thus the melt index ratio, becomes independent of IV. The same holds true with regards to shear rate as its effects, albeit much smaller than the temperature and IV effects, are similar in both the numerator and denominator of Equation (5) and thereby cancel each other out. Thus, the viscosity and melt index ratio are approximately constant over a wide range of IV. So, by measuring the viscosity ratio (or melt index ratio) at one IV, we can apply it to any other IV and calculate the 140°C melt index using the existing MI data at 190°C.

16. Following this procedure, a sample of AAPE having an IV of 0.60 dl/g was tested and found to have $MI(190^{\circ}C) = 435$ g/10min and $MI(140^{\circ}C) = 235$ g/10min. Thus the ratio is

$$MI(140^{\circ}C)/MI(190^{\circ}C) = \eta(190^{\circ}C)/\eta(140^{\circ}C) = 0.39 \quad (10)$$

17. The $MI(190^{\circ}C)$ data in Figure 2 can now be converted to $140^{\circ}C$ by multiplying it by 0.39. Combining equations (1), (5), and (10) above, we get a revised equation for the MI at $140^{\circ}C$:

$$MI(140^{\circ}C) = \frac{\eta(190^{\circ}C)}{\eta(140^{\circ}C)} MI(190^{\circ}C) = 0.39 * 38.3 IV^{-5.1} = 14.9 IV^{-5.1} \quad (11)$$

This equation is plotted in Figure 3. Application of this equation to the 0.8 to 1.6dl/g IV range of our current claims corresponds to a melt index range ($140^{\circ}C$) of 46.5 g/10min to 1.35 g/10min, respectively, which is outside the 50 to 400 g/10min MI range claimed by Masuda. Similarly, inspection of Figure 3 illustrates that polyesters with an IV greater than about 0.78 dl/g are outside the Masuda range. This should be expected since the materials prepared by Masuda are meant to be easy flowing for adhesive applications, whereas the polymers of our invention have to have sufficient viscosity to be handled by normal melt processing equipment.

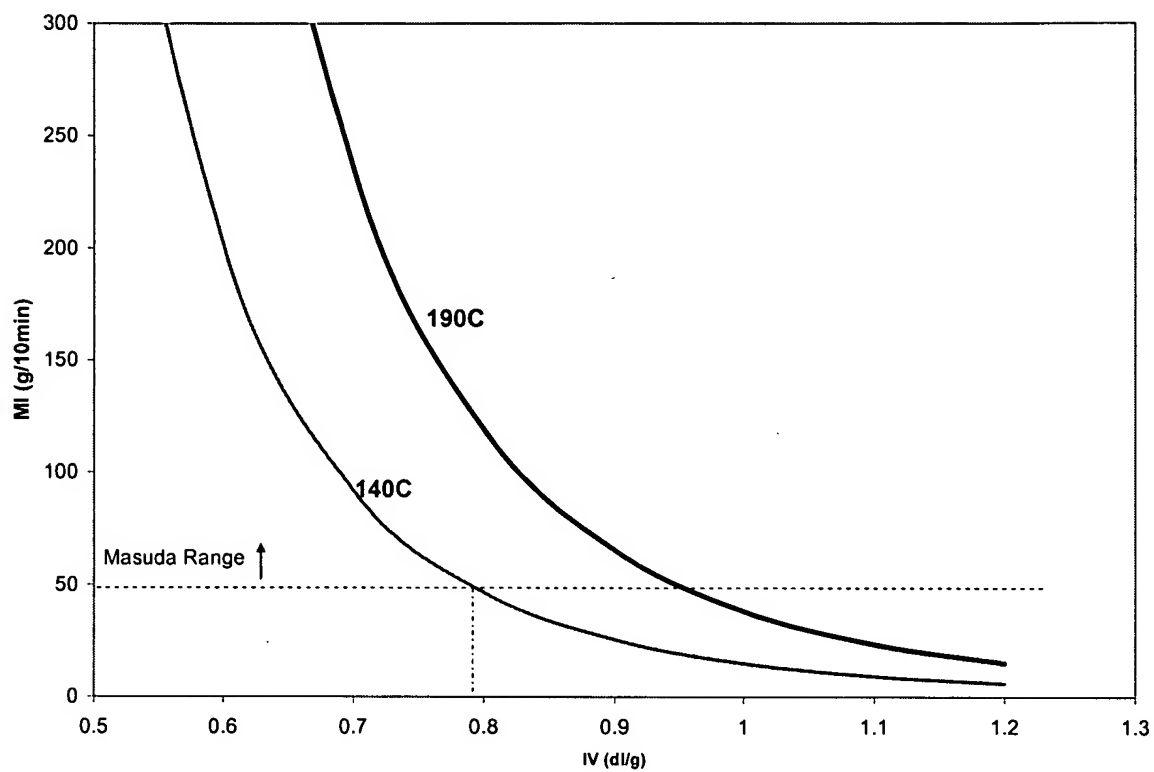


Figure 3. Melt Index Data Corrected to 140°C

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

November 21, 2006
Date

Marcus David Shelby Ph.D., P.E.
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